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A Study of the Binary System Na-Cs



A STUDY OF THE BINARY SYSTEM Na-Cs

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## I INTRODUCTION

Systems of two alkali metals have been little studied. Lithium in its alloy forming properties resembles magnesium rather than sodium, and its behavior is in some respects anomalous. Molten lithium is hardly miscible with sodium or potassium.<sup>(1)</sup> Sodium forms a single compound  $\text{Na}_2\text{K}$ , with potassium,<sup>(2)</sup> but this compound dissociates below its melting point. It is probable that both lithium and sodium would prove, on investigation, to form compounds with rubidium and caesium, but that the metals of the potassium sub-group would not combine with one another.

In the second sub-group, copper, silver, and gold alloy together, forming solid solutions either completely or to a limited extent. Sodium forms a single compound with gold  $\text{NaAu}_2$  melting without decomposition at  $989^\circ$ ,<sup>(3)</sup> whilst silver crystallizes in a pure state from its solution in molten silver.

This investigation was undertaken with the view of studying the temperature-concentration diagram of the system sodium-caesium.<sup>(3)</sup>

The only binary systems studied, in which caesium occurs are  $\text{Cs-Hg}$ ,<sup>(4)</sup> and  $\text{Cs-O}$ .<sup>(5)</sup>



## II SOURCE AND PURIFICATION OF MATERIALS

Sodium.- Electrolytic sodium, purified by treating it with naphta and amylalcohol, was used. After washing off the metal in a light fraction of naphta, it was weighed under oil.

Caesium.- The caesium was prepared from caesium chloride. The caesium chloride was obtained by the extraction of pol-lucite with concentrated hydrochloric acid. To this solution a calculated amount of iodine is added and then chlorine passed through. The dichloriodides of caesium, rubidium, and sodium are thereby precipitated from the solution. Caesium dichloriodide is the least soluble and precipitates first, then rubidium-, and last sodium dichloriodide. The caesium-dichloriodide is recrystallized from hot concentrated hydrochloric acid, and on drying heated in a casserole, so as to decompose it and to drive off the iodine-monochloride. The caesium chloride thus left, is recrystallized twice from conductivity water, into which HCl-gas may be passed.

On spectroscopic analysis the chloride then proved to contain traces of sodium only.

The caesium chloride was reduced with metallic calcium in vacuum at a bright red heat. The apparatus here used consisted of a Jena combustion tube, sealed off on one end, on the other end of which was sealed a test tube with side arm, and glass stopcock. The connection between the





two tubes was made with sealing wax. The combustion tube served as the reaction chamber, the test tube as the receiver for the metallic caesium. In order to prevent the Jena glass tube from being attacked by the calcium, the mixture was placed in an iron boat, which previously had been carefully reduced. The system was evacuated with the help of a Nelson vacuum oilpump, which was kept running during the entire reduction.

On heating the mixture, the metallic caesium soon starts distilling over, and has a bright silvery metallic lustre. It solidifies in the receiver at room temperature. As the process of reduction and the distillation of the metal goes on, however, the metal turns to a golden yellow and occasionally gets coated with a black precipitate, supposedly an oxide, which seems to dissolve into the metal and to cause the change in color. Also, with the change of color, lowering of the freezing-point occurs, and the metal melts in the receiver. This is in agreement with Rengade's work on the  
(5)  
binary system caesium-oxygen.

At each reduction the iron boat was charged with a mixture of one molecule caesium chloride and two molecules calcium (40 grams of caesium chloride and 20 grams of calcium). The average yield obtained was 65% of the theoretical yield (22 grams metallic caesium). High temperature and a considerable excess of calcium materially increase the yield.

The calcium used in this reduction was electrolytic calcium of the General Electric Company. It was shaved on



the lathe and ground up in a meat chopper.

It was observed that the metallic caesium on being treated with larger amounts of amylalcohol loses its golden yellow color and regains its original bright silvery lustre. At the same time a considerable raise of the freezing-point occurs. The amylalcohol therefore was used extensively for removing the caesium oxides and sub-oxides.

The caesium was handled in the following way:

A layer of naphta (boiling point  $208^{\circ}$  centigrade) was introduced through the side arm of the receiver, the receiver and the reaction-chamber then filled with dry nitrogen, freed from oxygen, and the connection between the combustion tube and the receiver broken. The metal was then heated to about  $120^{\circ}$  centigrade and treated with a mixture of naphta and amylalcohol, all impurities washed off with pure naphta, and finally the metal was cooled off. The metal was then cut up, weighed under oil and finally transferred into Jena glass tubes, about one centimeter in diameter, in which the heating and cooling curves were made.

The melts were protected as previously by a thin layer of oil to which again a few drops of amylalcohol were added. The amylalcohol in this case serves the purpose of getting a homogeneous melt. The metal otherwise reacts with the oil and becomes coated instantly with a film of the reaction product. The amylalcohol dissolves this film, cleans off the surface of the globules which can now run together





readily and form a homogeneous melt. Several authors mention that the specific gravity of the oil is responsible for preventing the globules from running together. It is our experience, however, that this trouble is chiefly caused by contamination of the metallic surface.



### III METHOD

(6)  
The well known method of thermal analysis of the alloys was applied.

Every melt consisted of 2.50 grams of alloy.

Cooling and heating curves were made by transferring the melts from an oil-bath at a constant temperature of  $140^{\circ}\text{C}.$ , into a mixture of solid carbondioxide and ether, which was kept at a constant temperature of  $-80^{\circ}\text{C}.$ , and vice versa. In this procedure, the melts were protected by an air-jacket.

The temperature readings were taken with a Siemens and Halske "Millivoltmeter für Temperaturmessungen", and a copper constantan thermocouple, calibrated with standardized mercury, - and pentane thermometers.



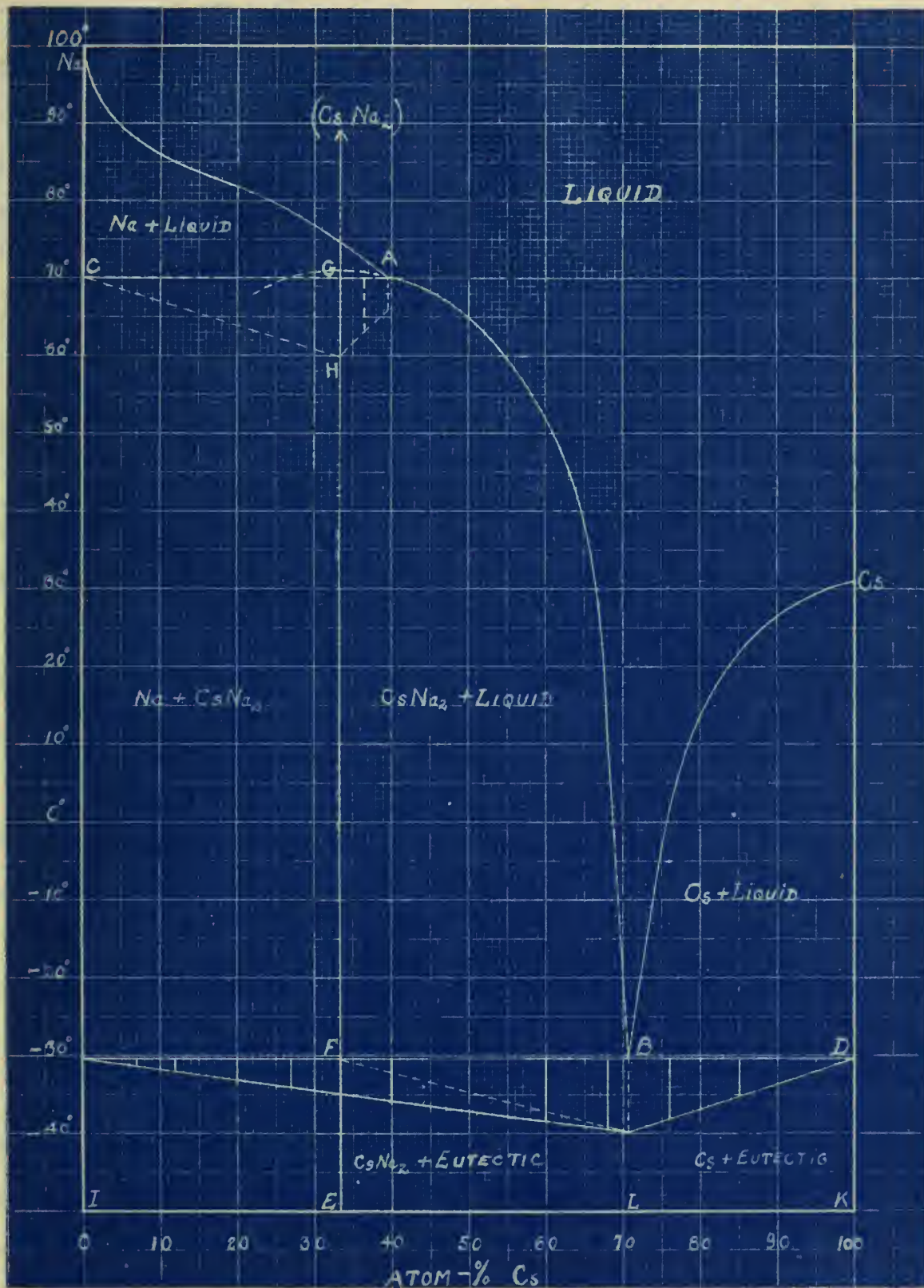
IV TABLE

		Temp. at beginning of crystallization	Eutectic Crystallization on cooling curves		
Atom-% Cs	Cooling curves	Heating curves	Temperature	Time in seconds	
0	98.7	98.3	-	0	
7	84.6	88.0	-30.4	11	
12	85.0	86.7	-30.4	15	
20	80.5	81.85	-30.0	31	
27	78.6	80.25	-30.6	40	
33.33	74.8	74.3	-30.4	58	
40	70.0	(77.9)	-30.0	57	
60	-	52.1	-30.0	56	
68	-	12.9	-30.4	91	
76	-	-	-30.4	93	
85	-	21.4	-32.4	40	
100	28.7	31.0	-	0	





V TEMPERATURE-CONCENTRATION DIAGRAM  
OF THE BINARY SYSTEM Na-Cs







## VI DISCUSSION OF DIAGRAM

The diagram shows a concealed maximum at a concentration of 33.33% Cs., corresponding to a compound  $\text{CsNa}_2$ .

The compound dissociates at its melting point. Extrapolation of its freezing-point curve BA gives  $71.0^\circ\text{C}$ . for the dissociation temperature.

On cooling the Cs-Na melts containing from 0% to 39.5% caesium, caesium crystals separate out. These crystals below  $70^\circ\text{C}$ ., react with the melt containing 39.5% caesium, and form the compound  $\text{CsNa}_2$ .

This reaction is not completed on cooling, however, as considerable eutectic crystallization still takes place at  $30.4^\circ\text{C}$ .

The reaction, however, can be completed by exposing these melts for several days at a temperature somewhat below the dissociation temperature.

If now the melts are cooled to  $-60^\circ$ , and heating curves are subsequently made - no more eutectic crystallization will be observed at  $-30.4^\circ\text{C}$ .

For melts containing 39.5% to 70.7% caesium - the time of eutectic crystallization will be greatly reduced by this procedure, as is indicated in the diagram by a dotted line.

These heating curves, for concentrations between 0% and 39.5% caesium, will further show thermal effects, due to the dissociation of the compound  $\text{CsNa}_2$  at the dissociation temperature. These thermal effects will be the largest for the con-



centration 33.33% caesium,--the characteristic concentration of the compound. This is suggested by the dotted time-of-dissociation diagram at 70°.

The compound breaks up at this temperature into Cs-crystals and liquid melt of the concentration A, which differs from the pure compound only in so far as it contains 6.2% more caesium. The curves BA and NaA further intersect at a very large angle. Consequently, the times of dissociation for melts between 33.33% and 40.0% caesium will not entirely become zero at A. On exposure.

The method of exposure has not been applied as yet. The investigation, however, is being completed in this direction. Extrapolation of the freezing-point curve of the compound, giving very distinct evidence of a maximum at the 33.33% caesium concentration is as far as the investigation has proceeded at present.

Thermal effects observed on the cooling curves cannot be used with success in determining the composition of the compound, as the reaction is not completed in cooling.

The intersection of the freezing-point curves, of  $\text{CsNa}_2$  and of Cs, and also the intersection of the observed times of eutectic crystallization, both give 70.7°Cs for the eutectic concentration.

The temperature-concentration diagram consists of the following fields:-

Above Na AB Cs	- liquid
In Na CA	-Na and liquid



In Cs DB	- Cs and liquid
In EFBL	- $\text{CsNa}_2$ and eutectic
In LBDK	- Cs and eutectic
In AGFB	- $\text{CsNa}_2$ and liquid
In ICGE	- Na and $\text{CsNa}_2$





## VII CONCLUSIONS

Amylalcohol is a suitable material for removing caesium-oxides from their solution in the metal.

The melting point of caesium was found to be  $31.0^{\circ}$ .

Previous authors mention:

(7)  
Setterberg,  $26.5^{\circ}$   
(8)  
Eckardt and Graefe,  $26.37^{\circ}$   
(4)  
Kurnakow and Zukowsky,  $25.3^{\circ}$   
(5)  
Rengade,  $28.25^{\circ}$ .

Of these Rengade is the most reliable as he has redistilled his metal in vacuum.

The only compound formed in the binary system Cs-Na is  $\text{CsNa}_2$ .





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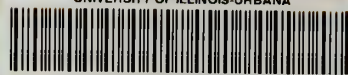
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